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(54) AQUEOUS HYDROGEN PEROXIDE FOR STERILIZATION

(57) The present invention provides a hydrogen peroxide solution for sterilization which has a hydrogen peroxide concentration of 30 to 45 % by weight, an Fe concentration of 2 ppb or less and an Al concentration of at least 15 ppb and in which a concentration of a stabilizer comprising orthophosphoric acid is 40 ppm at the most. The above hydrogen peroxide solution for sterilization is used for sterilizing vessels filled with beverages and foods and packaging materials in an aseptic filling equipment. The above hydrogen peroxide solution for sterilization has less evaporation residue, does not clog a narrow piping part such as a spray nozzle and therefore makes it possible to stably operate an aseptic filling equipment. Further, an austenite base stainless material can be used as a material for the transporting facilities and the tanks.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a hydrogen peroxide solution for sterilization which is heated and evaporated and in which hydrogen peroxide evaporated is used as a bactericide. More specifically, it relates to a hydrogen peroxide solution for sterilization which contains less amount of a stabilizer added to the hydrogen peroxide solution and is reduced in an amount of impurities to the utmost and which contains a specific additive component.

RELATED ART

[0002] In recent years, according to development of equipments in which beverages, foods and the like are aseptically filled into vessels and popularization of PET bottles, bactericides used for aseptic filling which are excellent in handling have come to be desired. A method in which a hydrogen peroxide solution is evaporated by heating to a boiling point thereof or higher in an evaporator and in which a gas of hydrogen peroxide is sprayed together with air to sterilize a vessel is known as a sterilizing method using a hydrogen peroxide solution (refer to a patent document 1). However, involved therein are the problems that a part of a stabilizer added to a hydrogen peroxide solution is adhered and remains onto a spray nozzle and an evaporator to clog a narrow piping part and that stable operation of an aseptic filling equipment is disturbed.

[0003] Stabilizers are added to a hydrogen peroxide solution used for industrial uses and food additives in order to inhibit the hydrogen peroxide solution from being decomposed by decomposing components contained therein. Substances having an ability to form a coordinate compound or a chelate compound with decomposing components, for example, Fe are used for a stabilizer, and a method in which pyrophosphoric acid salts are used in combination with inorganic compounds such as orthophosphoric acid has so far been known. Known is a method in which an amount of substances adhered onto a spray nozzle and an evaporator is reduced by controlling the addition amounts of the above compounds (refer to a patent document 2). However, involved therein is the problem that an inhibition in an amount of a stabilizer leads to an increase in risks such as loss of hydrogen peroxide by decomposition and abnormal decomposition thereof in transportation and storage in tanks. Further, involved therein is the problem that an austenite base stainless material used for parts such as a nozzle, a filling unit and the like which are brought into contact with a hydrogen peroxide solution is reacted with a stabilizer having an ability to form a chelate compound and results in eluting Fe, Cr and the like to increase decomposition of hydrogen peroxide.

[0004] A semiconductor grade hydrogen peroxide solution scarcely contains hydrogen peroxide decomposing components, and a stabilizer is not added thereto. Accordingly, solved is the problem that the stabilizer is adhered and remains onto a spray nozzle and an evaporator and clogs a narrow piping part to disturb stable operation of an aseptic filling equipment. However, the semiconductor grade hydrogen peroxide solution is required to use high grade materials for delivering, transporting and receiving facilities and the like, and sufficient attentions and high costs are required for handling it.

Patent document 1: Japanese Patent Application Laid-Open No. 47242/1999
Patent document 2: Japanese Patent Application Laid-Open No. 152116/1998

DISCLOSURE OF THE INVENTION

[0005] An object of the present invention is to provide a hydrogen peroxide solution for sterilization which solves the foregoing problems in conventional techniques and enables stable operation of an aseptic filling equipment and which can stably be transported and stored even in transporting facilities and tanks made by using an austenite base stainless material.

[0006] Intensive researches repeated by the present inventors on relation among an amount of a stabilizer added to a hydrogen peroxide solution, the kind of the stabilizer, an evaporation residue, impurities contained, stability and the like have resulted in finding that use of a hydrogen peroxide solution which has an Fe concentration of 2 ppb or less and an Al concentration of at least 15 ppb and to which orthophosphoric acid is added as a stabilizer so that a whole addition amount thereof is 40 ppm at the maximum makes it possible to reduce an amount thereof which is adhered and remains onto a spray nozzle and an evaporator and stably operate an aseptic filling equipment without clogging a narrow piping part. Further, they have found that in the above hydrogen peroxide solution, hydrogen peroxide is scarcely decomposed during transportation and storage even in transporting facilities and tanks made by using an austenite base stainless material. The present inventors have reached the present invention based on the above knowledges.

[0007] That is, the present invention relates to a hydrogen peroxide solution for sterilization which is used in an aseptic filling equipment and which sterilizes a vessel or a packaging material by hydrogen peroxide vapor, wherein a hydrogen

peroxide concentration is 30 to 45 % by weight; an Fe concentration is 2 ppb or less; an Al concentration is at least 15 ppb; and a concentration of a stabilizer comprising at least orthophosphoric acid is 40 ppm at the most. Further, the present invention relates to a sterilizing method for a vessel or a packaging material using an aseptic filling equipment, comprising a step in which the above hydrogen peroxide solution for sterilization is heated and evaporated and in which resulting hydrogen peroxide vapor is brought into contact with the above vessel or packaging material.

BEST MODE FOR CARRYING OUT THE INVENTION

[0008] In the present invention, a hydrogen peroxide solution which is not a semiconductor grade can be used. The hydrogen peroxide solution of the present invention for sterilization has a hydrogen peroxide concentration of 30 to 45 % by weight. In the present invention, a stabilizer (sodium pyrophosphate and orthophosphoric acid) in which a safety and an effectiveness are confirmed and which is designated as an additive for foods by Minister of Health, Labor and Welfare is preferably added to the hydrogen peroxide solution, and only orthophosphoric acid is particularly preferably added as the stabilizer.

[0009] An addition amount of the stabilizer is preferably as small as possible, and considering inactivation of hydrogen peroxide decomposing components contained in a general purpose hydrogen peroxide solution and clogging of a narrow piping part, it is 40 ppm at the most, preferably 1 to 40 ppm. If it exceeds 40 ppm, a spray nozzle for spraying vaporized hydrogen peroxide onto a vessel or a packaging material is frequently clogged by the stabilizer contained in the hydrogen peroxide solution for sterilization, and a removing work for adhered matters is required, which results in disturbing stable operation of an aseptic filling equipment. On the other hand, if the stabilizer is not added, a stability of hydrogen peroxide is deteriorated to bring about abnormal decomposition, and a problem on the safety is caused. In the present application, %, ppm and ppb are based on a weight in all cases.

[0010] Heavy metals are known as decomposing components for a hydrogen peroxide solution, and decomposing components contained in a hydrogen peroxide solution which is industrially produced are limited almost to Fe, Cr, Ni and Pd. In the hydrogen peroxide solution of the present invention for sterilization, the concentrations of Ni and Pd each are controlled preferably to 0.1 ppb or less, more preferably 0.01 to 0.1 ppb. Further, the concentrations of Fe and Cr each are controlled preferably to 2 ppb or less, more preferably 0-1 to 2 ppb. In the present invention, the Fe concentration is controlled particularly preferably to 2 ppb or less. A method for controlling the Fe concentration to 2 ppb or less includes a method in which the hydrogen peroxide solution is brought into contact with a cation exchange resin or an anion exchange resin and a method in which the hydrogen peroxide solution is heated and vaporized to condense and refine hydrogen peroxide-containing steam.

[0011] In the hydrogen peroxide solution of the present invention for sterilization, an Al concentration is at least 15 ppb, preferably 15 to 1000 ppb, more preferably 15 to 300 ppb and further preferably 15 to 200 ppb. A method for controlling the Al concentration to at least 15 ppb includes a method in which the hydrogen peroxide solution is brought into contact with a cation exchange resin or an anion exchange resin and a method in which the hydrogen peroxide solution is heated and vaporized to condense and refine hydrogen peroxide-containing steam.

[0012] The hydrogen peroxide solution of the present invention for sterilization is used particularly preferably for sterilizing vessels and packaging materials in aseptic filling of beverages, foods and the like. A sterilizing unit constituting a part of an aseptic filling equipment comprises at least a hydrogen peroxide-supplying part, an evaporator equipped with a heating device and a spray nozzle. The structure thereof shall not specifically be restricted, and publicly known equipments, for example, the equipments described in the patent documents 1 and 2 described above can be used.

[0013] The hydrogen peroxide solution for sterilization which has been introduced from the hydrogen peroxide-supplying part into the evaporator is vaporized by heating at a temperature of a boiling point thereof or higher, preferably the boiling point to 200°C by the heating device. The vaporized hydrogen peroxide solution for sterilization moves to a downstream side in the evaporator by compressed air introduced from the hydrogen peroxide-supplying part or a supplying part which is independent from this, and it is sprayed onto a vessel or a packaging material from the spray nozzle disposed at an end of a downstream side in the evaporator. The gaseous hydrogen peroxide solution sprayed is cooled and condensed to be turned into mists, and they are adhered on the surface of the vessel or the packaging material in the form of fine droplets to exhibit a bactericidal action. The vessel or the packaging material subjected to bactericidal treatment is dried and sent to an aseptic filling step for beverages, foods and the like.

[0014] The hydrogen peroxide solution of the present invention for sterilization contains Al and orthophosphoric acid. Al and orthophosphoric acid have a function to form a passive coating film of aluminum phosphate on the surface of an austenite base stainless material and reduce elution of Fe, Cr and Ni to thereby inhibit hydrogen peroxide from being decomposed-Accordingly, the austenite base stainless material such as SUS304, 304L, 316 and 316L is preferably used as a material for parts in the stabilizing unit which are brought into contact with the above hydrogen peroxide solution for sterilization.

EXAMPLES

[0015] Next, the present invention shall be explained in further details with reference to examples and comparative examples. However, the present invention shall not be restricted by the following examples. The Al concentrations, the Fe concentrations and the Cr concentrations were measured by atomic absorption analysis, and the others were measured according to JIS K-1463.

[0016]

(1) Hydrogen peroxide concentration
Determined by titrating with an N/10 potassium permanganate aqueous solution.
(2) stability
A fixed amount of the sample was heated in a boiling water bath for 5 hours. After cooling down, water was added thereto to adjust the volume to that before heating, and then hydrogen peroxide was immediately determined to calculate the stability (%) according to the following equation:

$$H = (J'/J) \times 100$$

(wherein H is the stability (%); J' is the hydrogen peroxide concentration after heated for 5 hours; and J is the hydrogen peroxide concentration before heated).
(3) Al concentration
Measured by atomic absorption analysis.
(4) Fe concentration
Measured by atomic absorption analysis.
(5) Cr concentration
Measured by atomic absorption analysis
(6) Evaporation residue
The sample 250 g was taken in a beaker, and a platinum piece was put therein to decompose hydrogen peroxide. Thereafter, the decomposed solution was transferred into a platinum dish and evaporated and dried up on a water bath, and then the residue was dried at 105 to 110°C for 2 hours. After left cooling in a desiccator containing silica gel, a weight of the residue was measured to calculate the evaporation residue (ppm) according to the following equation:

$$C = (D/S) \times 10^6$$

(wherein C is the evaporation residue (ppm); D is an amount (g) of the residue; and S is an amount (g) of the sample taken.

Examples 1 to 2 and Comparative Examples 1 to 4

[0017] A hydrogen peroxide concentration of the prescribed hydrogen peroxide solution was adjusted to about 35 % by weight. A prescribed amount of the stabilizer was added thereto to obtain the respective sample hydrogen peroxide solutions, and the respective items thereof were measured. The results thereof are shown in Table 1.

Table 1

	Addition amount of stabilizer		Measurement results					
	85 % H_3PO_4 ppm	$Na_4P_2O_7 \cdot 10\,H_2O$ ppm	H_2O_2 %	Stability %	Al ppb	Fe ppb	Cr ppb	Evaporation residue ppm
Example 1	8	0	35.29	98.72	17	1	<1	7
Example 2	21	0	35.29	99.12	19	1	<1	18
Comparative Example 1	6	4	35.29	99.74	19	1	<1	7

(continued)

	Addition amount of stabilizer		Measurement results					
	85 % H_3PO_4 ppm	$Na_4P_2O_7 \cdot 10\,H_2O$ ppm	H_2O_2 %	Stability %	Al ppb	Fe ppb	Cr ppb	Evaporation residue ppm
Comparative Example 2	15	10	35.29	99.85	15	1	<1	20
Comparative Example 3	30	19	35.30	99.85	16	1	<1	39
Comparative Example 4	0	0	35.29	97.34	20	1	<1	<1

[0018] Next, the respective samples 330 g were taken in a polyethylene vessel having a volume of 1 L, and a SUS304L piece (pre-treatment: washing for degreasing→dipping in 30 % nitric acid for 3 hours→washing with water→air drying, size: 30 × 40 × 4 mm, surface area: 0.00296 m^2) was put therein and stored at room temperature while dipping. During the storage, only the hydrogen peroxide solution was exchanged with new one after 7 days and 14 days passed since starting dipping. The hydrogen peroxide solutions taken out after 21 days passed were used to measure the same items as described above. The results thereof are shown in Table 2.

Table 2

	Measurement results					
	H_2O_2 %	Stability %	Al ppb	Fe ppb	Cr ppb	Evaporation residue ppm
Example 1	35.24	85.24	18	4	1	7
Example 2	35.27	85.45	17	5	1	19
Comparative Example 1	35.25	69.90	20	65	16	6
Comparative Example 2	35.27	88.99	19	59	15	20
Comparative Example 3	35.26	91.80	20	92	21	40
Comparative Example 4	34.91	78.68	17	6	1	<1

Examples 3 to 6 and Comparative Examples 5 to 6

[0019] A hydrogen peroxide concentration of the prescribed hydrogen peroxide solution was controlled to about 35 % by weight. The prescribed amounts of the stabilizer and aluminum nitrate were added thereto to prepare the respective sample hydrogen peroxide solutions, and the respective items thereof were measured. The results thereof are shown in Table 3.

Table 3

	Aluminum nitrate (reduced to Al atom) ppb	85 % H_3PO_4 ppm	H_2O_2 %	Stability %	Al ppb	Fe ppb	Cr ppb
Comparative Example 5	0	2	35.25	99.94	<1	<1	<1
Comparative Example 6	0	5	35.24	99.91	<1	<1.	<1
Example 3	50	2	35.23	99.91	60	<1	<1
Example 4	50	5	35.21	99.97	56	<1	<1
Example 5	100	2	35.21	99.88	116	<1	<1
Example 6	100	5	35.20	99.97	109	<1	<1

[0020] The respective samples 330 g were taken in a polyethylene vessel having a volume of 1 L, and a SUS304L piece (pre-treatment: washing for degreasing-dipping in 30 % nitric acid for 3 hours→washing with water→air drying, size: 30 × 40 × 4 mm, surface area: 0.00296 m^2) was put therein and stored at room temperature while dipping. During the storage, only the hydrogen peroxide solution was exchanged with new one after 7 days and 14 days passed since starting dipping. The hydrogen peroxide solutions taken out after 21 days passed were used to measure the same items as described above. The results thereof are shown in Table 4.

Table 4

	H_2O_2 %	Stability %	Al ppb	Fe ppb	Cr ppb
Comparative Example 5	35.15	88.96	<1	4	<1
Comparative Example 6	34.17	89.84	<1	4	<1
Example 3	35.15	92.20	56	3	<1
Example 4	35.18	94.05	58	4	<1
Example 5	35.18	99.26	117	1	<1
Example 6	35.17	98.83	115	3	<1

INDUSTRIAL APPLICABILITY

[0021] The present invention makes it possible to stably operate an aseptic filling equipment without allowing a part of stabilizer added to the hydrogen peroxide solution to be adhered and remain onto a spray nozzle and an evaporator to clog a narrow piping part such as a nozzle. Further, if using transporting facilities and tanks made by using an austenite base stainless material, hydrogen peroxide is scarcely decomposed, and therefore the hydrogen peroxide solution can stably be transported and stored.

Claims

1. A hydrogen peroxide solution for sterilization which is used in an aseptic filling equipment and which sterilizes a vessel or a packaging material by hydrogen peroxide vapor, wherein a hydrogen peroxide concentration is 30 to 45 % by weight; an Fe concentration is 2 ppb or less; an Al concentration is at least 15 ppb; and a concentration of a stabilizer comprising at least orthophosphoric acid is 40 ppm at the most.

2. A sterilizing method for a vessel or a packaging material using an aseptic filling equipment, comprising a step in which the above hydrogen peroxide solution for sterilization is heated and evaporated and in which resulting hydrogen peroxide vapor is brought into contact with the above vessel or packaging material.

3. An aseptic filling equipment using the hydrogen peroxide solution for sterilization as described in claim 1, wherein a material of a part brought into contact with the above hydrogen peroxide solution for sterilization is an austenite base stainless material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/309709

A. CLASSIFICATION OF SUBJECT MATTER
B65B55/10(2006.01), ***C01B15/01***(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B65B55/10, C01B15/01-15/037

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11-035306 A (Mitsubishi Gas Chemical Co., Inc.), 09 February, 1999 (09.02.99), Par. Nos. [0003] to [0009], [0015] to [0017], [0024] (Family: none)	1,3
X	JP 10-258811 A (Toppan Printing Co., Ltd.), 29 September, 1998 (29.09.98), Claim 7; Par. No. [0029]; Fig. 1 (Family: none)	2

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 June, 2006 (29.06.06)	11 July, 2006 (11.07.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/309709

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The invention of claims 1 and 3 relates to an aqueous hydrogen peroxide for sterilization whose usage and components are specified and to an aseptic filling apparatus wherein use is made of the aqueous hydrogen peroxide.

The invention of claim 2 relates to a method of sterilizing a container or packaging material by means of hydrogen peroxide vapor.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee..

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 11047242 A **[0004]**
- JP 10152116 A **[0004]**